PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in Processes of High Vacuum-short Path Distillation

We, EASTMAN KODAK COMPANY, a Company organised under the laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, State of New York, United States of America (Assignees of KENNETH CLAUDE DEVEREUX HICKMAN, a British subject, of Kodak Park, Rochester, County Monroe, State of New York, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in processes of high vacuum-short path distillation, particularly that specific form of high vacuum-short path distillation in which the distance separating evaporating and condensing surfaces is equal to or less than the mean free path of the molecules of the distilland, herein referred to as molecular distillation.

Processes of high vacuum-short path distillation are well known and have been applied to the distillation and purification of various materials. Thus, Burch U.S. Patent Specification 1,955,321 discloses the molecular distillation of hydrocarbon oils and in U.S. Patents specifications 1,823,569 and 1,949,893 Hickman has disclosed the similar distillation of vegetable and animal oils, fats, and waxes in order to concentrate therapeutic agents contained therein. Process of high vacuum-short path distillation have been applied to the treatment of numerous other types of materials such as sterols, hormones, etc. and materials containing same. The materials so treated are often of a viscous character, of high molecular weight and therefore do not flow with sufficient rapidity through the still. This results in overheating and decomposition of valuable constituents and is especially disastrous when materials containing heat sensitive substances such as vitamins are treated. Often the materials to be distilled contain dissolved substances which are thrown out of solution on distillation of part of the solvent and this material deposits on the heated evaporating surface where it continues to collect resulting in clogging of the apparatus. Where the constituents of the mixture to be distilled boil at nearly the same temperature the entire liquid may evaporate leaving a deposit of non-volatile residue on the evaporating surface. As the evaporating and condensing surfaces are arranged in close proximity the deposit cannot be effectively removed unless the whole still is dismantled which involves considerable loss in time and expense. A clean evaporating surface is important for efficient distillation, and it has been necessary until the advent of this invention to periodically dismantle the still and mechanically remove deposited materials.

This invention has for its object to overcome the deficiencies of hitherto known high vacuum-short path distillation processes by providing a process in which viscous material or materials yielding vitamins, sterols, hormones or unsaturated glycerides and tending to deposit solid substances can be distilled without clogging of the distillation apparatus and without decomposition of heat sensitive materials contained therein. A remedy is also sought for preventing deposition of non-volatile substances in high vacuum-short path distillation processes when the constituents of the mixtures being distilled have closely allied boiling points.

According to the present invention, substances which are liquid at the temperature of the still and which on distillation yield vitamins, sterols, hormones or unsaturated glycerides, are subjected to high vacuum-short path distillation, there being added to the original distilland or a fraction thereof still requiring distillation, another liquid having a vapour pressure lower than that of the distillate under the conditions appertaining, thereby preventing deposition of non-volatile residuum upon the distilling surface tending to clog the still.

It has already been proposed to subject finely-divided solid materials to molecular distillation by mixing them with a liquid serving as a vehicle or carrier, e.g.

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the high vacuum-short path distillation of solid placenta, dispersed in an oil, so as to yield a fraction containing the female sex hormone, has already been proposed but in our process the liquid diluent is added to a distilland which is itself liquid at the temperature of the still, for the purpose of accelerating the flow of the liquid over the distilling surface, for example, by lowering the viscosity or surface tension of the distilland.

In the following examples and description several of the preferred embodiments of the invention are set forth, but it is to be understood that they are included merely for purposes of illustration and not as a limitation thereof.

For achieving the best results by means of the present invention a liquid should be selected which is miscible with the distilland, since the precipitation of solids will be more effectively prevented. However, non-miscible or partially miscible liquids may be used since they dissolve precipitated solids or will mechanically entrain and remove precipitated solids which are not soluble therein. The selection of the liquid agent obviously depends upon the character of the particular distilland and the vapour pressure of the distillate to be removed. Where the distillate has a relatively low vapour pressure the liquid need not have an excessively low volatility. It is important, however, to select a liquid which has a lower vapour pressure than the distillate or it will also distil giving no beneficial results as far as the removal of solids is concerned. Preferably a liquid is employed which also has a considerably lower vapour pressure than the distilland especially where contamination of the distillate by the entraining agent is undesirable.

In speaking of substances having a relatively high or low volatility it is to be understood that this invention relates to high vacuum-short path distillation and in such processes materials generally recognized as being of low volatility are usually distilled and the comparison is therefore between substances which are considered to be relatively non-volatile under conditions of normal temperature and pressure but which may have appreciable and comparable volatilities when subjected to the high temperature and low pressures associated with high vacuum-short path distillation. Thus, in distilling a substance such as propylene glycol which has a relatively high volatility in the field of high vacuum distillation, a liquid having a lower vapour pressure such as triphenyl phosphate may be employed to prevent deposition. The phoshate has a vapour pressure which is also rather high but is sufficiently low to enable distillation of the glycol without substantial contamination. In distilling those natural vegetable and animals oils which serve as sources of vitamins, sterols, hormones, or unsaturated glycerides, substantially no residue is left to carry away dissolved solids and protein matter. As such oils consisting substantially of glycerides have a low volatility it is necessary to add a liquid agent which has a very low vapour pressure. The particular agent selected depends upon the nature of the glyceride or oil to be treated and where the glyceride to be distilled is of rather high volatility as compared with other glycerides the latter may be used as the liquid agents. Thus, in distilling linseed, salmon or cottonseed oil, a glyceride of very low volatility such as castor oil may be added.

Instead of using a foreign liquid it is often convenient to use the lowest vapour pressure fraction of the oil which is to be distilled. Most unsaturated natural oils contain a small quantity of extremely non-volatile liquid residue. If this residue passes too slowly over the heated surface of the still it may dry down in spite of its low volatility or it may decompose or polymerize. By increasing the rate of travel through the still especially at the hottest portions this non-volatile residue mixed with constituents which it is desired to volatilize can be easily withdrawn and partially or entirely returned to some previous position or stage of the still. It may thus be added to the original oil to be distilled or to the hot columns which it is desired to lubricate. In this way any desired proportion of non-volatile liquid may be accumulated and recirculated.

The proportions of liquid agent used are not critical and may be several times the weight of the distilland or only a fraction thereof depending upon the physical characteristics of the material to be distilled, the amount of solids dissolved therein and their tendency to precipitate, and upon the amount of the distilland which is to be removed as distillate, tendency to polymerize etc. Where the distilland is viscous and contains a high proportion of dissolved solid or gelatinous material, a higher proportion must be used such as equal proportions, or in some cases 2, 5 or as high as 25 parts or more of liquid to 1 of distilland. The same is true where substantially all of the liquid portion of the distilland is to be removed as distillate.

Lower proportions such as about .5 to 50% are satisfactory in cases where the material treated is of low viscosity and/or little of it is to be removed as distillate. It is emphasized that the proportions vary according to the nature of the distilland and that proportions cannot therefore be empirically defined. However, anyone skilled in the art can, by following the directions given, apply the principles of the invention to any particular material under consideration.

Where heating of the distilland causes deposition of solids a solvent for the solids may be employed as the distilland diluent. This expedient is effective even where there is normally a considerable portion of the distilland remaining as undistilled liquid.

The distilland diluent employed may be separated from the distilland and re-used any desired number of times. In order to make this separation easier it is often desirable to employ a liquid which is immiscible with the distilland at ordinary or sub-normal temperatures, but is miscible therewith at the temperature of distillation. Such a liquid can be separated from the distilland for re-use by the simple expedient of cooling and separation of the two layers of liquid thus formed.

EXAMPLE.

Linseed oil is subjected to molecular distillation at temperatures between 150° C. and 225° C., four fractions being withdrawn at successively higher temperatures, the first and second fractions each representing 10%, the third 30% and the final fraction all but 5% of the oil. It is found that the remaining 5% will not spread evenly over the heated columns of the still and that it gathers into local streams where it polymerizes and dries down to a hard varnish. The rate of flow is increased by introducing fresh linseed oil into the still more quickly and a relatively large quantity (10—30%) of viscous undistilled oil is withdrawn from the bottom of the last column and is pumped up and admixed with oil from the previous stages which is entering this column. Five percent of this viscous oil coming from the bottom of the last column is led to waste. Distillation of all but 5% of the original oil is thus achieved and yet a quantity equal to 10—30% of the original oil is maintained in rapid and satisfactory circulation over the last column on which the deposition of solids is greatly diminished.

The process of this invention is especially applicable to those distillation processes which occur under such high vacuum conditions that a high proportion of the vaporized molecules do not return to the evaporative surface and are condensed upon a surface located in close proximity to the evaporating surface. This distance is usually of the order of, or less than the mean free path of the molecules of residual gas. Processes employing a distance of less than about the mean free path are processes of molecular distillation. Very useful results can be obtained, however, using distances of several times this amount if a rapid renewal of the evaporating surface is maintained. In such a case the distillate is carried to the condensing surface at least in part by convection. Such a process may be termed pseudo-molecular distillation. Processes of molecular distillation can conveniently be carried out in any of the various types of molecular distillation apparatus. The materials to be distilled are preferably first degassed after addition of the entraining liquid by either of the two methods previously disclosed. The material may be degassed by being passed through a chamber or series of chambers suitably evacuated by pumps or it may be subjected to contact with an inert gas, counter-current or otherwise, and heated or otherwise, when the absorbed gases are swept out by the inert gas, and the material then subjected to vacuum distillation to remove the inert gases without the latter having a detrimental influence upon the properties of the therapeutic substances contained in the material. However, this mode of treatment is unnecessary and the material to be distilled may be entirely run into a distillation chamber and degassed and distilled therein, or the distilland can be admitted relatively slowly directly into the distillation chamber, the chamber being provided with large ducts and high vacuum pumps to withdraw the air and gases and easily volatilizable materials contained therein. By this latter method the withdrawal of gases, etc., is accomplished so rapidly that the pressure of the residual gas in the vessel during distillation is substantially the same as when the degassing step is carried out in a separate chamber. In a preferred method the material to be distilled is passed through the still a number of times or through a number of successive stills and each time the temperature is raised and/or the pressure lowered so as to remove successively the less and less volatile constituents.

In molecular distillation processes a low pressure usually less than .1 mm. is employed, resulting in an appreciable mean free path. Pressures of less than about .01 mm. such as for instance, about

.001 mm. to .0001 mm. are preferred. However, as the mean free path is inversely proportional to the pressure it is apparent that the higher the degree of vacuum, the greater will be the rate of distillation. It is therefore possible to use evaporating and condensing surfaces situated within one inch at a residual operating pressure of less than 3 microns mercury or within a quarter of an inch at less than 1 microns mercury, or within 10 inches at less than .3 microns mercury and so forth. With pressure and distance as interchangeable quantities in molecular distillation no real lower limit to the pressure or upper limit to the distance can be defined, but for reasons of expediency it is preferable not to operate with a residual gas pressure of less than .01 microns mercury or a distance of greater than 10 ft. Distances of less than about 10 inches such as ½ inch to 6 inches have been found to be most suitable.

In selecting the temperatures to be used in high vacuum short path and especially molecular distillation processes consideration must be given to the character of the material to be distilled and of pressures used. Materials of very low volatility must be heated to temperatures approaching their decomposition point even though the lowest pressures attainable are employed. With such compounds temperatures as high as 329° C. are useful. On the other hand the separation of easily volatilizable compounds can be effected at low temperatures such as at room temperatures or slightly higher such as up to about 70° C. Most materials have vapour pressures intermediate between these two extreme types and they may be satisfactorily distilled at temperatures of 70° to 300° C. and usually at lower temperatures of between 70° and 250° C. The latter range and especially those temperatures between 90° and 230° C. have been found to be most satisfactory for the distillation of vitamins from vitamin containing oils.

While the invention has been described as being especially applicable to processes of molecular distillation it is applicable to all processes of high vacuum-short path distillation where a troublesome problem in circulation of a distilland of the kind as herein before defined and clogging of apparatus is encountered. It is, however, especially useful in processes of molecular distillation since the evaporating surfaces are necessarily very large and it is important to distribute the distilland thereon in a thin layer.

The materials used as diluents of the distilland may be any organic compounds or mixtures thereof which have the requisite physical properties as regards vapour pressure, and viscosity. Thus glycerides such as castor oil, and olein, phthalates such as benzyl, butyl, amyl, and octyl phthalate, high boiling alcohols such as mono, di and tri glyceral, esters such as triacetin, methyl oleate, and stearate, high boiling hydrocarbons such as lubricating oil, "Apiezon" oils, etc., may be employed. Obviously no liquid should be selected which has a high viscosity or decomposes at the temperature at which it is employed.

As already stated the process of the invention is applicable to the high vacuum-short path distillation of any substances containing vitamins, sterols, hormones or unsaturated glycerides which have a high viscosity or tendency to deposit solids on the evaporating surface. Examples of materials to which the invention has been applied, in addition to those given above are the distillation of crude animal and vegetable oils, fats and waxes as hereinbefore defined, such as linseed, walnut, soya menhaden, cottenseed, wheat germ, salmon, cod-liver, herring, halibut, mackerel, etc., to recover unsaturated glycerides and/or therapeutic agents such as fat soluble vitamins and sterols; crude germinal gland hormone concentrates and synthetic reaction mixtures containing them.

It is to be understood that the term liquid agent designates materials which are liquid under normal conditions as well as those materials which are viscous liquids or solids under normal conditions but which readily flow at the temperature of the still.

The herein described process affords an economical simple and effective solution of the vexatious problem of preventing deposited solids from clogging or lowering the efficiency of a high vacuum-short path still. By means of the invention viscous and deposit-forming materials may be rapidly run through a molecular still and evenly spread in a thin layer over the evaporating surface without thermal decomposition or deposition of solids.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The process of short path-high vacuum distillation of substances which are liquid at the temperature of the still and which on distillation yield fractions containing vitamins, sterols, hormones or unsaturated glycerides, in which there is added to the original distilland or a fraction obtained therefrom still requiring

distillation another liquid having a vapour pressure lower than that of the distillate under the conditions appertaining, thereby preventing deposition of non-volatile residuum upon the distilling surface, tending to clog the still.

2. The process as claimed in claim 1 applied specifically to substances which are normally liquids.

3. The process as claimed in claim 1 or 2 carried out under conditions of molecular distillation.

4. The process as claimed in claim 1, 2 or 3 in which the distilland diluent is separated from the distilland remaining after distillation and then recycled.

5. The process as claimed in claim 4 in which a distilland diluent is used which is miscible with the distilland when hot, but immiscible when cold.

6. The process as claimed in claim 1, 2 or 3 in which a non-volatile liquid fraction of the original distilland is recirculated, at least in part, to serve as the distilland diluent.

7. The process as claimed in claims 1, 2 or 3 in which the original distilland diluent comprises a mixture of a liquid having a vapour pressure lower than that of the distillate and a non-volatile liquid distilland fraction remaining from a previous "run".

Dated this 12th day of February, 1937

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